

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 811 625 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:  
10.12.1997 Bulletin 1997/50

(51) Int Cl.6: C07D 487/04, C07D 519/00,  
C09B 57/00  
// (C07D487/04, 209:00, 209:00)

(21) Application number: 97810324.0

(22) Date of filing: 27.05.1997

(84) Designated Contracting States:  
CH DE ES FR GB IT LI NL

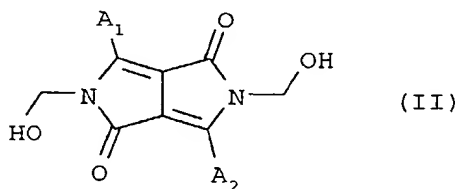
(71) Applicant: Ciba Specialty Chemicals Holding Inc.  
4057 Basel (CH)

(30) Priority: 05.06.1996 US 19138 P  
26.09.1996 US 27469 P  
26.09.1996 US 27470 P

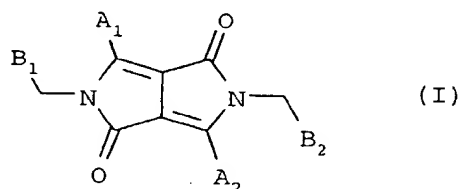
(72) Inventor: Hendi, Shivakumar Basalingappa  
Newark, DE 19702 (US)

(54) Process for preparing diketopyrrolopyrrole derivatives

(57) This disclosure relates to a process for preparing bis(hydroxymethyl)pyrrolopyrrole compounds of the formula



wherein  $A_1$  and  $A_2$  are aryl radicals, by reacting a 1,4-diketopyrrolopyrrole with formaldehyde or paraformaldehyde. The compound of formula (II) can be isolated or further reacted in a one pot synthesis to yield a compound of the formula



wherein  $B_1$  and  $B_2$  are organic radicals.

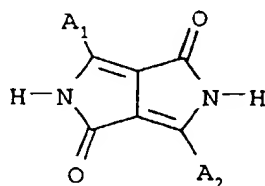
EP 0 811 625 A2

## Description

This application relates to a process for preparing 1,4-diketo-3,6-diarylpyrrolopyrrole derivatives wherein a diketopyrrolopyrrole is reacted with formaldehyde or paraformaldehyde to yield a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione which is isolated or further reacted.

Further, this application relates to a process wherein a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione is reacted with a precursor of organic radicals  $B_1$  and  $B_2$ , a process wherein the precursor of the organic radicals  $B_1$  and  $B_2$  is a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole or a quinacridone, a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione, a process for its preparation, a diketopyrrolopyrrole derivative having two quinacridone radicals as substituents, a diketopyrrolopyrrole derivative having two diaryldiketopyrrolopyrrole radicals as substituents, a pigment composition, a method of reducing the viscosity of a dispersion, and a method of preparing a basecoat/clearcoat finish.

Diaryldiketopyrrolopyrroles of the formula



wherein  $A_1$  and  $A_2$  are aryl radicals are well-known as important pigments.

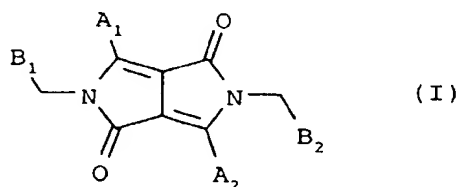
U.S. Patent No. 4,585,878 discloses N-substituted derivatives of the diaryldiketopyrrolopyrrole pigments, which are useful as polymer soluble dyes or as pigments, wherein the N-substituent does not confer solubility in water. According to U.S. Patent No. 4,585,878, the N-substituted derivatives of the diaryldiketopyrrolopyrrole pigments are prepared by reacting a diaryldiketopyrrolopyrrole compound in an organic solvent with a compound containing the ultimate N-substituents attached to a leaving group, or by reacting 2 moles of a compound of the formula  $R-N=CH-A$ , wherein R is the N-substituent and A is an aryl group, or one mole each of two different compounds of the formula  $R-N=CH-A$ , with a succinic acid diester in the presence of a base and an organic solvent and then dehydrogenating the product.

Rheology-improving agents for organic pigments reduce the viscosity of a dispersion of the organic pigment in a high-molecular-weight organic material. Some compounds capable of functioning as rheology-improving agents for organic pigments are known. For example, phthalimidomethylquinacridone, quinacridone monosulfonic acid salts, especially the aluminum salt, the dimethylaminopropylsulfonamide derivative of quinacridone and pyrrolylmethylquinacridone are known rheology improving agents for organic pigments.

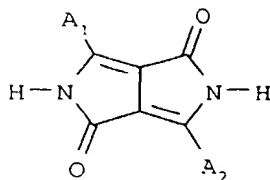
Although the known rheology improving agents adequately reduce the viscosity when the organic pigment is dispersed in a high-molecular-weight organic material, the incorporation of the known rheology improving agents in a pigment composition based on a bright red or highly saturated orange pigment generally results in unacceptable pigmentary properties with significant loss in color and color saturation.

Hence, it was the object of the present invention to provide rheology improving agents which do not show the abovementioned drawbacks. Preferably, the rheology improving agents should be based on N-substituted diaryldiketopyrrolopyrroles.

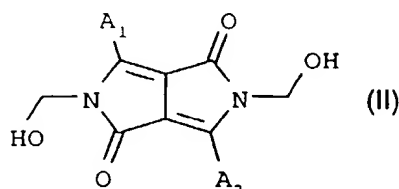
Accordingly a process for the preparation of a diketopyrrolopyrrole derivative of the formula (I)



was found, wherein  $A_1$  and  $A_2$  are identical or different aryl radicals and B<sub>1</sub> and B<sub>2</sub> are identical or different organic radicals; which diketopyrrolopyrrole derivative contains from 0 to 6 moles of  $-SO_3M$  per mole of diketopyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation, which process comprises a reaction wherein a 1,4-diketo-3,6-diarylpyrrolopyrrole of the formula



is reacted in a first step with formaldehyde or paraformaldehyde to yield a sulfonated or non-sulfonated intermediate of the formula



which reacts in a second step with a precursor of the organic radicals,  $B_1$  and  $B_2$ , to yield the diketopyrrolopyrrole derivative of formula (I).

Further, a process, wherein a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione is reacted with a precursor of organic radicals  $B_1$  and  $B_2$ , a process wherein the precursor of the organic radicals  $B_1$  and  $B_2$  is a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole or a quinacridone, a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione, a process for its preparation, a diketopyrrolopyrrole derivative having two quinacridone radicals as substituents, a diketopyrrolopyrrole derivative having two diaryldiketopyrrolopyrrole radicals as substituents, a pigment composition, a method of reducing the viscosity of a dispersion, and a method of preparing a basecoat/clearcoat finish were found, too.

The present invention relates to a process for preparing a variety of N-substituted derivatives of diaryldiketopyrrolopyrrole pigments wherein the N-substituents are linked to the diaryldiketopyrrolopyrrole by  $-CH_2-$  or  $-O-CH_2-$  linkages. The inventive process involves reacting a diaryldiketopyrrolopyrrole with formaldehyde or paraformaldehyde to yield a 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione intermediate and further reacting the intermediate, with or without isolation, with a second reactant which reacts with the hydroxymethyl groups. The products of the reaction are useful as colorants and as rheology improving agents for pigment dispersions. The 2,5-bis(hydroxymethyl)-3,6-diarylpyrrolopyrrole-1,4-dione intermediate is useful as a synthon for the preparation of a variety of DPP derivatives, and as a stabilizer for polymers.

In general, the second reactant reacts with the compound of formula (II) by a substitution reaction or to form an  $-O-$  linkage.

The first step is preferably carried out by adding the 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole to a solution of paraformaldehyde in concentrated sulfuric acid, preferably having a  $H_2SO_4$  concentration greater than 90 percent by weight, most preferably above 95 percent by weight.

In general, the stoichiometric amount of formaldehyde or paraformaldehyde (calculated as formaldehyde) is used in the first step. Thus, the molar ratio of the 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole to the formaldehyde or paraformaldehyde (calculated as formaldehyde) during the first step usually is in the range of 0.75:2 to 1.25 to 2, preferably 1:2.

After the first step is complete, the resulting intermediate is reacted with the precursor to yield the diketopyrrolopyrrole derivative of formula (I).

Preferably, both steps are carried out at a temperature of from 20 to 100°C. If a high degree of sulfonation is desired, the process is carried out at higher temperatures, for example above 40°C. If it is desirable to have a low degree of sulfonation, the reaction is maintained at a lower temperature, preferably 40°C or below.

After the reaction is complete, the 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole derivative usually is isolated by procedures conventionally used in the art for isolating 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrroles, in particular by pouring the sulfuric acid solution into ice water maintaining the temperature below 10°C and stirring the resulting aqueous slurry for about 1 hour, followed by filtration, washing and drying to yield the 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole derivative in solid form.

Since it is not necessary to isolate the intermediate, the inventive process is preferably a one pot process. However, it is possible to isolate the intermediate prior to carrying out the second step, especially, for example, in those instances where it is desired to carry out the second step in a solvent other than the solvent used for the first step.

Suitable solvents for the second step include concentrated sulfuric acid, polyphosphoric acid and organic solvents which do not react with the compound of formula (II), especially polar organic solvents such as acetonitrile, benzonitrile,

dimethylformamide, dimethylsulfoxide, tetramethylenesulfone.

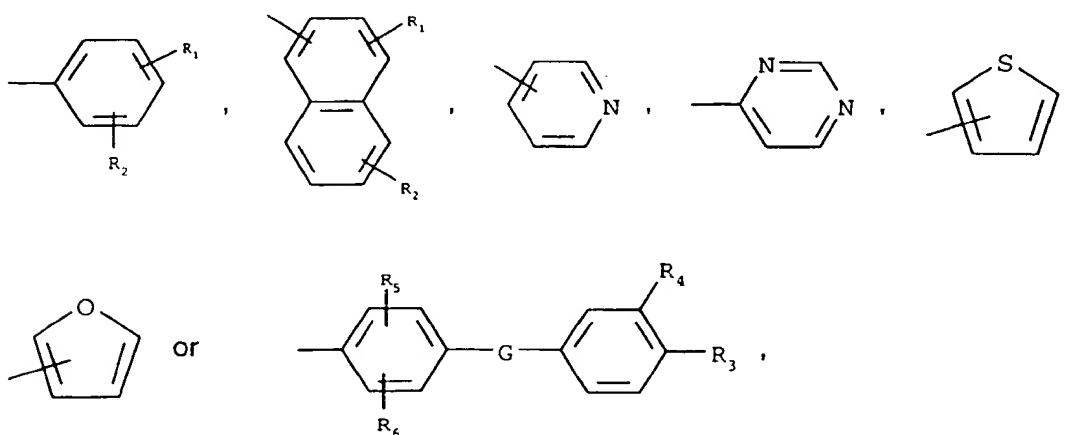
It is also possible to carry out the second step in a solvent which reacts with the compound of formula (II) to yield the desired product, for example, C<sub>1</sub>-C<sub>10</sub> alcohols are suitable solvents if the compound of formula (I) is the ether obtainable by reacting the compound of formula (II) with the alcohol.

In a preferred embodiment of the present invention a 1,4-diketo-3,6-diarylpyrrolopyrrole of the formula (II) is reacted with a precursor of the organic radicals, B<sub>1</sub> and B<sub>2</sub>.

Preferably, the diketopyrrolopyrrole derivatives of formula (I) contain from 0 to 4 moles of -SO<sub>3</sub>M per mole of diketopyrrolopyrrole derivative; most preferably from 0 to 2 moles per mole of diketopyrrolopyrrole derivative. In general, if the reaction is carried out at about 40-50°C, the product contains about 0.5 moles of -SO<sub>3</sub>M per mole of diketopyrrolopyrrole derivative.

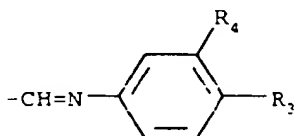
M is preferably hydrogen, or an alkali metal, such as sodium or potassium, an alkaline earth metal, such as magnesium, an aluminum, a zinc or an ammonium cation. Examples of suitable ammonium cations include quaternary ammonium cations, such as trimethylcetylammmonium or tributylbenzylammmonium.

A<sub>1</sub> and A<sub>2</sub> as aryl include both aromatic and heteroaromatic radicals. Radicals which are particularly suitable as A<sub>1</sub> and A<sub>2</sub> include radicals of the formula



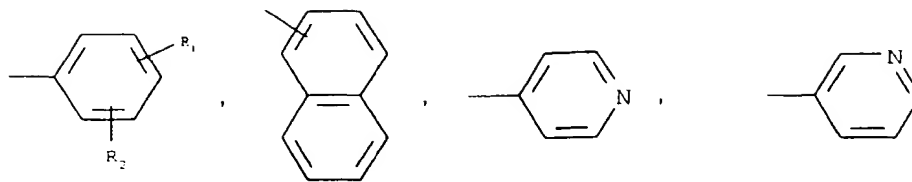
wherein

R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen, halogen, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkylmercapto, C<sub>1</sub>-C<sub>18</sub>alkylamino, C<sub>1</sub>-C<sub>18</sub>alkoxycarbonyl, C<sub>1</sub>-C<sub>18</sub>alkylaminocarbonyl, -CN, -NO<sub>2</sub>, trifluoromethyl, C<sub>5</sub>-C<sub>6</sub>cydoalkyl, -CH=N-(C<sub>1</sub>-C<sub>18</sub>alkyl), phenyl,

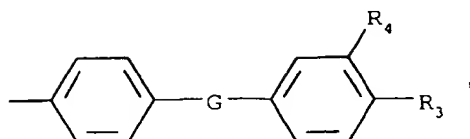


imidazolyl, pyrazolyl, triazolyl, piperazinyl, pyrrolyl, oxazolyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, morpholinyl, piperidinyl or pyrrolidinyl, G is -CH<sub>2</sub>-, -CH(CH<sub>3</sub>)-, -C(CH<sub>3</sub>)<sub>2</sub>-, -CH=N-, -N=N-, -O-, -S-, -SO-, -SO<sub>2</sub>-, -CONH- or -NR<sub>7</sub>-, R<sub>3</sub> and R<sub>4</sub> are each independently of the other hydrogen, halogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy or -ON, R<sub>5</sub> and R<sub>6</sub> are each independently of the other hydrogen, halogen or C<sub>1</sub>-C<sub>6</sub>alkyl, and R<sub>7</sub> is hydrogen or C<sub>1</sub>-C<sub>6</sub>alkyl.

In particular, A<sub>1</sub> and A<sub>2</sub> are each a group of formula



or



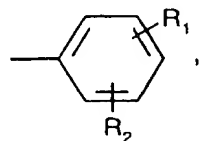
wherein

$R_1$  and  $R_2$  are each independently of the other hydrogen, chloro, bromo,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_6$ alkoxy,  $C_1$ - $C_6$ alkylamino, phenyl or CN.

G is -O-, -NR<sub>7</sub>-, -N=N- or -SO<sub>2</sub>-.

$R_3$  and  $R_4$  are hydrogen, and  $R_7$  is hydrogen, methyl or ethyl.

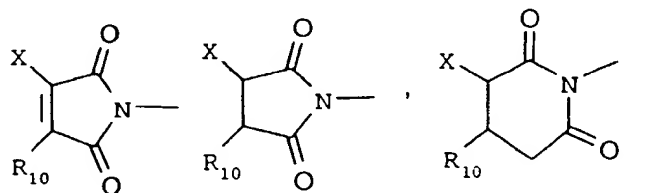
and more particularly  $A_1$  and  $A_2$  are each a group of formula

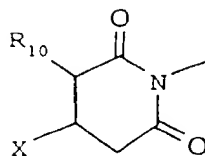


wherein  $R_1$  and  $R_2$  are each independently of the other hydrogen, methyl, tert-butyl, chloro, bromo, phenyl or CN. At least one of  $R_1$  and  $R_2$  is preferably hydrogen. Most preferably, at least one of  $R_1$  and  $R_2$  is hydrogen and the other is in the 3- or 4 position of the phenyl ring.

According to the present invention, the organic radicals  $B_1$  and  $B_2$  are derivable from a precursor which reacts with the hydroxy groups of a compound of the formula (II) either by a substitution reaction or to form an -O-linkage.

Precursors which react with a hydroxyl group by a substitution reaction are generally compounds which comprise an aromatic radical, a heteroaromatic radical, or radicals of the formulae  $X-C(=O)-Y$ -,  $-Y-C(=O)-O-X$ ,  $X-C(=S)-Y$ -,  $-Y-C(=S)-O-X$ ,  $-Y-C(=S)-S-X$ ,  $X-C(=N)-Y$ -,  $XZN$ -,  $X-S$ -,  $X-SO_2$ -,  $X-SO_2-NR_{10}$ -,

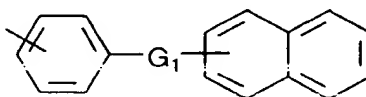




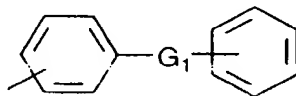
and  $-N(R_{10})-C(=O)-O-X$ ; wherein X and Z are each hydrogen or an aliphatic, alicyclic, araliphatic, aromatic or heterocyclic radical, or X and Z together form a 3 to 8 membered ring, Y is the residue of an active methylene containing moiety, and  $R_{10}$  is hydrogen, an aliphatic radical, an alicyclic radical, an araliphatic radical, an aromatic radical or a heterocyclic radical, or  $R_{10}$  and X together form a 3 to 8 membered ring.

Examples of  $B_1$  and  $B_2$  radicals derivable from a precursor which reacts with a hydroxyl group to form an -O-linkage include an alkyl halide and radicals of the formulae  $X-C(=O)O-$ ,  $X-C(=S)O-$ ,  $X-SO_2-O-$ ,  $XO-$ ; wherein X has the meaning given above.

As aromatic radicals,  $B_1$  and  $B_2$  especially include radicals containing 1, 2, 3, 4 or more phenyl rings which are bonded directly to each other, bonded to each other through a linking group, fused, or any combination thereof. The biphenyl radical is an example of two phenyl rings directly bonded to each other. Radicals of the formula



and



wherein  $G_1$  is a linking group, are examples of phenyl rings bonded through each other through a linking group. Examples of aromatic radicals containing fused phenyl rings include naphthyl, anthryl and phenanthryl.

The linking group  $G_1$  is especially those linking groups described above for the variable G.

As heteroaromatic radicals,  $B_1$  and  $B_2$  especially include radicals containing one or more 5, 6 or 7 membered aromatic rings containing from 1 to 4 heteroatoms. In general, the heteroatom(s) are nitrogen, oxygen, sulfur or any combination thereof. Suitable heteroaromatic radicals include the pyrrolopyrroles, especially the 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrroles and quinacridones.

Preferably, Y is the residue of an active methylene containing moiety. Active methylene moieties are generally those methylene groups which are linked to an electron withdrawing substituent, such as a carbonyl or nitrile substituent. In general, active methylene moieties participate in a Mannich type or similar reaction. In general, Y is  $-CHX$ ,  $-CH_2-X$ ,  $-(CH=CH)_n-CH_2-X$ , wherein n is 1, 2 or 3. When Y is the  $-CHX-$  radical, the  $-CHX-$  radical is part of a ring, for example, when  $B_1$  or  $B_2$  is the  $X-C(=O)-Y-$  radical, X and Y can form part of, for example, a cyclohexanone ring.

X and Z usually are aliphatic, alicyclic, araliphatic, aromatic or heterocyclic radicals.

In general, aliphatic radicals include  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  alkenyl, and  $C_1$ - $C_{10}$  alkynyl radicals, including straight and branched chains.

Alicyclic radicals include those moieties containing only one or more nonaromatic hydrocarbon rings. Important alicyclic radicals include radicals derived from  $C_3$ - $C_8$  cycloalkanes and  $C_3$ - $C_8$  cycloalkenes. Examples of important alicyclic radicals include cyclopentyl, cyclohexyl and cycloheptyl. Alicyclic radicals also include those moieties wherein there is, for example, a  $-C(=O)-$  on the ring, such as cyclohexanone.

Araliphatic radicals are those moieties which contain an aliphatic portion and an aromatic portion, for example a phenyl or heteroaromatic portion. Examples of araliphatic radicals include radicals derived from the phenylalkanoic acids, the naphthylalkanoic acids, the pyridine alkanic acids, the quinoline alkanic acids, the indole alkanic acids, such as those derived from phenyl acetic acid, phenyl propionic acid, or indole acetic acid.

Aromatic radicals suitable as X and Z include those described above as being useful as  $B_1$  and  $B_2$ . The term "aromatic" radical, in this instance, does not include heteroaromatic radicals.

Heterocyclic radicals contain one or more nonaromatic and/or aromatic rings which contain one or more heteroatoms: especially 3 to 8 membered rings which contain 1 to 3 heteroatoms, which heteroatoms are especially nitrogen, sulfur and oxygen. The term heterocyclic radical includes fused ring systems wherein one or more rings contain one or more heteroatoms. Important heterocyclic radicals include pyridinyl, pyranil, tetrahydrofuranyl, morpholino, pyrimidinyl, pyrone, oxazine, azepinyl, triazinyl, oxathiazinyl, pyrrolyl, benzofuranyl, piperazinyl, oxathiazolyl, oxadiazolyl, quinolinyl, indolyl, carbazolyl, xanthenyl, acridinyl, coumarinyl, benzoxazolyl, benzopyrone, quinazolinyl. Heterocyclic radicals include those wherein the ring is a lactone or a lactam.

The description of radicals above also defines aliphatic, alicyclic, araliphatic, aromatic and heterocyclic radicals suitable as  $R_{10}$ . When  $R_{10}$  combines with X to form a ring, the ring is preferably a five or six membered ring.

The aromatic, heterocyclic, aliphatic, alicyclic and araliphatic radicals are unsubstituted (by any group other than hydrogen) or substituted by one or more, preferably 0 to 4, customary substituents.

Customary substituents include hydroxy, carbonyl, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkylmercapto,  $C_1$ - $C_{18}$ alkylamino, di( $C_1$ - $C_{18}$ alkyl)amino,  $C_1$ - $C_{18}$ alkoxycarbonyl,  $C_1$ - $C_{18}$ alkylaminocarbonyl, -CN, -NO<sub>2</sub>, trifluoromethyl,  $C_5$ - $C_6$ cydoalkyl, -C=N-( $C_1$ - $C_{18}$ alkyl), phenyl, wherein alkyl groups can be further substituted by hydroxyl, halogen, nitro,  $C_1$ - $C_6$ alkoxy, carbonyl, -CN.

Substituents defined as halogen are typically iodo, fluoro, bromo and, preferably, chloro;

$C_1$ - $C_6$ alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, tert.-amyl, hexyl, and  $C_1$ - $C_{10}$ alkyl and  $C_1$ - $C_{18}$ alkyl are in addition typically heptyl, octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl.

$C_1$ - $C_{18}$ Alkoxy, also in  $C_1$ - $C_{18}$ alkoxycarbonyl, is typically methoxy, ethoxy, n-propoxy, isopropoxy, butoxy, hexyloxy, decyloxy, dodecyloxy, hexadecyloxy or octadecyloxy.

$C_1$ - $C_{18}$ Alkylmercapto is, for example, methylmercapto, ethylmercapto, propylmercapto, butylmercapto, octylmercapto, decylmercapto, hexadecylmercapto or octadecylmercapto.

$C_1$ - $C_{18}$ Alkylamino is, also in  $C_1$ - $C_{18}$ alkylaminocarbonyl, typically methylamino, ethylamino, propylamino, hexylamino, decylamino, hexadecylamino or octadecylamino.

$C_5$ - $C_6$ Cydoalkyl is typically cyclopentyl and cyclohexyl.

Important radicals containing the residue of an active methylene, Y, include radicals derivable from various acetacetanilides, cyanoacetanilides and benzoylacetanilides, such as ethylacetacetate, ethyl malonate, ethyl cyanoacetate, ethyl benzoyl acetate and malononitrile.

Important radicals of the formula  $X-C(=O)-O-$  include esters derivable from  $C_1$ - $C_{24}$  aliphatic acids, such as acetic acid, stearic acid, oleic acid, linoleic acid, acrylic acid, methacrylic acid or trifluoroacetic acid, a  $C_1$ - $C_{24}$  araliphatic acid, such as benzoic acid, phenyl acetic acid, phenyl propionic acid or indole acetic acid, a resin acid, such as abeitic acid, behemic acid, a naphthenic acid, a dimeric acid, wherein the aliphatic acids and araliphatic acids are unsubstituted or substituted by one or more customary substituents.

Important radicals of the formula  $X-C(=O)NR_{10}-$  and  $X-SO_2-NR_{10}-$  include those derivable from amides and sulfonamides prepared from an aliphatic amine and an aliphatic carboxylic or sulfonic acid, an aromatic amine and an aliphatic carboxylic or sulfonic acid, or an aromatic amine and an aromatic or araliphatic carboxylic or sulfonic acid. Suitable radicals of the formula  $X-C(=O)NR_{10}-$  and  $X-SO_2-NR_{10}$  especially include those wherein X is  $C_1$ - $C_{24}$  alkyl, phenyl, benzyl, tolyl, naphthyl and  $R_{10}$  is hydrogen, methyl, ethyl, n-propyl, isopropyl, phenyl, benzyl.

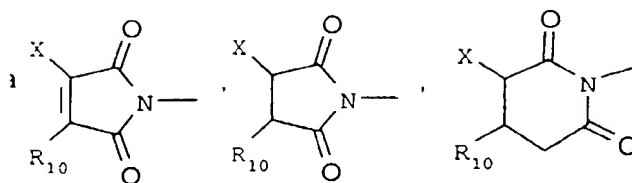
Important radicals of the formulae  $X-SO_2-$ ,  $X-SO_2-O-$  and  $X-C(=S)-O-$  include those wherein X is a  $C_1$ - $C_{24}$  aliphatic radical, an  $C_6$ - $C_{18}$  aromatic radical, a  $C_1$ - $C_{24}$  araliphatic radical, a 5, 6 or 7 membered heterocyclic ring, or a fused ring system containing a 5, 6 or 7 membered heterocyclic ring, such as pentyl, hexyl, phenyl, benzyl, tolyl, naphthyl, pyridinyl or indolyl. Important radicals of the formula  $X-SO_2-O-$  include those derivable from p-toluene sulfonic acid, naphthalene sulfonic acid, pentane sulfonic acid or a water-soluble dye which contains a -SO<sub>3</sub>H water-solubilizing group.

Important radicals of the formula XZN- include those derivable from N,N-di  $C_1$ - $C_{24}$ alkyl amines, such as dimethylamine, diethylamine dipropylamine, and dibutylamine, arylamines, such as N,N-diphenylamine, aralkylamines, such as N,N-dibenzylamine or ethylphenylamine, or heteroaryl amines, such as aminopyridine. The formula XZN- also includes those radicals wherein X and Z, together, along with the nitrogen atom, form a 3 to 8 membered ring, especially a 5 or 6 membered ring, such as a piperazine, morpholine, thiomorpholine, pyrrolidine or piperidine ring.

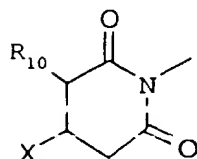
Important radicals of the formulae XO- include those wherein X is a  $C_1$ - $C_{24}$  aliphatic radical, a  $C_5$ - $C_{10}$  alicyclic radical, phenyl, benzyl, naphthyl, or a radical  $H-(CH_2CHR_{11}O)_m-CH_2CHR_{11}-$ , wherein  $R_{11}$  is hydrogen or methyl, especially hydrogen, and m is a number from 1 to 20.

Important radicals of the formula XS- include those wherein X is a  $C_1$ - $C_{24}$  aliphatic radical, a  $C_5$ - $C_{10}$ alicydic radical, phenyl, benzyl and naphthyl.

Important radicals of the formula



or



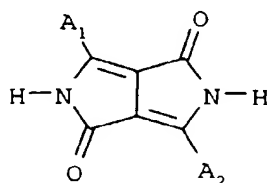
include radicals derivable from succinimide, glutarimide, phthalimide, naphthalimide and isoquinoline-1,3-dione.

Important radicals of the formula  $-N(R_{10})-C(=O)-O-X$  include those wherein  $R_{10}$  is hydrogen,  $C_1$ - $C_6$ alkyl, phenyl or benzyl, especially hydrogen and  $C_1$ - $C_6$ alkyl, and X is  $C_1$ - $C_6$ alkyl, for example, urethane.

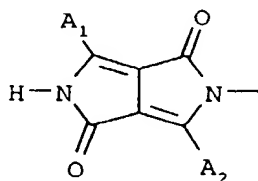
Aromatic and heteroaromatic radicals derivable from known dyes, such as azo, azomethine, or fiber-reactive dyes, for example triazine dyes, or known organic pigments, such as diketopyrrolopyrrole, quinacridone, phthalocyanine, indanthrone, isoindoline, isoindolone, flavanthrone, pyranthrone, anthraquinone, thioindigo, perylene and dioxazine pigments are suitable radicals for  $B_1$  and  $B_2$ . Quinacridinyl (derived from a quinacridone) and 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrolyl (derived from a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole) radicals are especially suitable radicals for  $B_1$  and  $B_2$ .

Thus, an aspect of the present invention relates to a process of preparing diketopyrrolopyrrole derivatives of the formula (I) wherein  $B_1$  and  $B_2$  are each a pigment moiety, in particular, a diketopyrrolopyrrole, quinacridone, phthalocyanine, indanthrone, isoindoline, isoindolone, flavanthrone, pyranthrone, anthraquinone, thioindigo, perylene and dioxazine pigment moiety.

1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrolyl radicals are especially suitable radicals for  $B_1$  and  $B_2$ . Such radicals are derivable from compounds of the formula



which are well-known as pigments, preferably

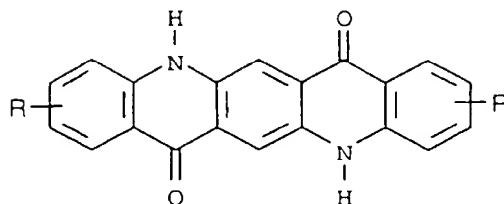


is used as radical.

When  $B_1$  and  $B_2$  are 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrolyl radicals, the preferences described above for  $A_1$  and  $A_2$  apply.

Another aspect of this invention relates to a process for preparing diketopyrrolopyrrole derivatives of formula (I) wherein  $B_1$  and  $B_2$  are quinacridinyl radicals. Such radicals are derivable from the compounds of the formula

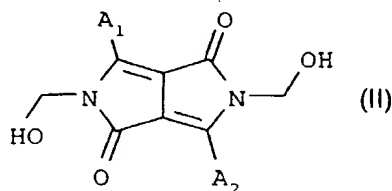




wherein each R is independently hydrogen, halogen, carboxyl, unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> alkyl which is substituted by halogen, unsubstituted C<sub>1</sub>-C<sub>6</sub> alkoxy, or C<sub>1</sub>-C<sub>6</sub> alkoxy which is substituted by halogen.

B<sub>1</sub> and B<sub>2</sub> are especially radicals derivable from quinacridone, 2,9-dichloroquinacridone, 4,11-dichloroquinacridone, 2,9-dimethylquinacridone, 4,11-dimethylquinacridone, 2,9-difluoroquinacridone.

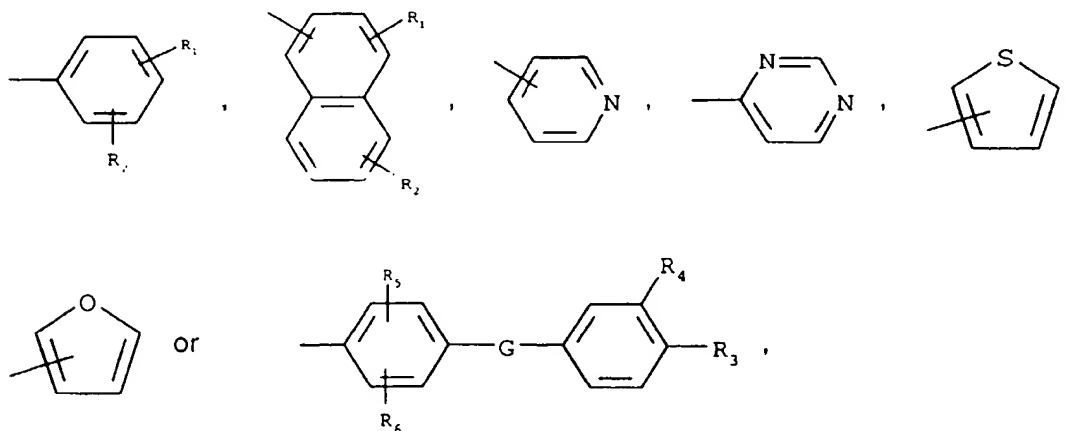
The present invention also relates to a compound of the formula



which contains from 0 to 6 moles of -SO<sub>3</sub>M per mole of the compound, wherein A<sub>1</sub> and A<sub>2</sub> are identical or different aryl radicals and M is hydrogen or a metal or ammonium cation.

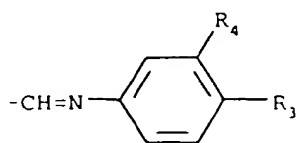
A<sub>1</sub> and A<sub>2</sub> have the meaning given above.

Preferably A<sub>1</sub> and A<sub>2</sub> are radicals of the formula



wherein

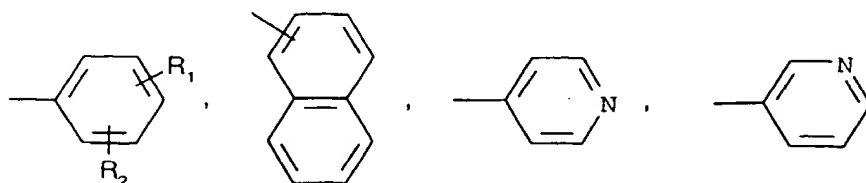
R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen, halogen, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkylmercapto, C<sub>1</sub>-C<sub>18</sub>alkylamino, C<sub>1</sub>-C<sub>18</sub>alkoxycarbonyl, C<sub>1</sub>-C<sub>18</sub>alkylaminocarbonyl, -CN, -NO<sub>2</sub>, trifluoromethyl, C<sub>5</sub>-C<sub>6</sub>cydoalkyl, -CH=N-(C<sub>1</sub>-C<sub>18</sub>alkyl), phenyl,



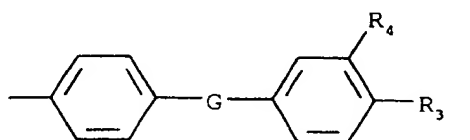
imidazolyl, pyrazolyl, triazolyl, piperazinyl, pyrrolyl, oxazolyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, morpholinyl, piperidinyl or pyrrolidinyl.

G is  $-\text{CH}_2-$ ,  $-\text{CH}(\text{CH}_3)-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{CH}=\text{N}-$ ,  $-\text{N}=\text{N}-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{SO}-$ ,  $-\text{SO}_2-$ ,  $-\text{CONH}-$  or  $-\text{NR}_7-$ .  $\text{R}_3$  and  $\text{R}_4$  are each independently of the other hydrogen, halogen,  $\text{C}_1$ - $\text{C}_6$ alkyl,  $\text{C}_1$ - $\text{C}_6$ alkoxy or  $-\text{CN}$ ,  $\text{R}_5$  and  $\text{R}_6$  are each independently of the other hydrogen, halogen or  $\text{C}_1$ - $\text{C}_6$ alkyl, and  $\text{R}_7$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl.

In particular,  $\text{A}_1$  and  $\text{A}_2$  are radicals of the formula



or



wherein

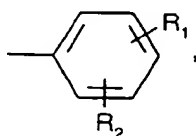
$\text{R}_1$  and  $\text{R}_2$  are each independently of the other hydrogen, chloro, bromo,  $\text{C}_1$ - $\text{C}_4$ alkyl,  $\text{C}_1$ - $\text{C}_6$ alkoxy,  $\text{C}_1$ - $\text{C}_6$ alkylamino, phenyl or CN.

G is  $-\text{O}-$ ,  $-\text{NR}_7-$ ,  $-\text{N}=\text{N}-$  or  $-\text{SO}_2-$ .

$\text{R}_3$  and  $\text{R}_4$  are hydrogen, and

$\text{R}_7$  is hydrogen, methyl or ethyl.

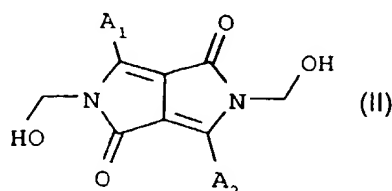
Most preferably,  $\text{A}_1$  and  $\text{A}_2$  are radicals of the formula



wherein  $\text{R}_1$  and  $\text{R}_2$  are each independently of the other hydrogen, methyl, tert-butyl, chloro, bromo, phenyl or CN. Preferably, at least one of  $\text{R}_1$  and  $\text{R}_2$  is hydrogen.

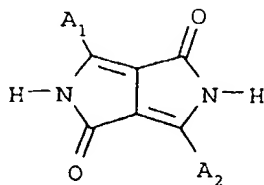
Preferably the compounds of formula (II) have from 0 to 4 moles of  $-\text{SO}_3\text{M}$ , most preferably from 0 to 2 moles of  $-\text{SO}_3\text{M}$ .

The present invention further relates to a process for preparing a compound of the formula



which contains from 0 to 6 moles of  $-\text{SO}_3\text{M}$  per mole of the compound, wherein  $\text{A}_1$  and  $\text{A}_2$  are identical or different aryl

radicals and M is hydrogen or a metal or ammonium cation, which process comprises reacting a 1,4-diketo-3,6-diarylpyrrolopyrrole of the formula



with formaldehyde or paraformaldehyde.

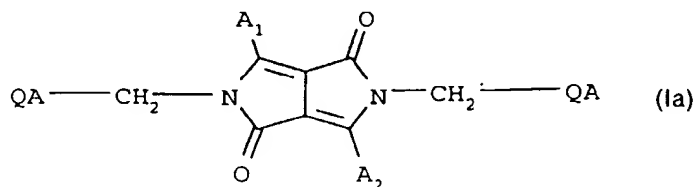
The preferences discussed above relating to the first step of the process for preparing the compounds of formula (I) are applicable to this aspect of the invention, too.

In particular, the present invention relates to the process wherein the 1,4-diketo-3,6-diarylpyrrolopyrrole is combined with paraformaldehyde in concentrated sulfuric acid; especially wherein the 1,4-diketo-3,6-diarylpyrrolopyrrole and formaldehyde (or paraformaldehyde, calculated as formaldehyde) are present in a molar ratio in the range of 0.75:2 to 1.25:2, most preferably of about 1:2.

If less sulfonation is desired, the reaction preferably is carried out at a temperature of 40°C or below. The reaction generally proceeds at higher temperatures, for example, in the range from about 20 to 120°C, but higher temperatures generally lead to a higher degree of sulfonation; which may be desirable depending on the intended use of the final product.

The hydroxymethyl derivative of formula (II) is generally isolated by precipitation and filtration, for example by drowning in an organic solvent or water followed by filtration.

Another preferred aspect of the present invention relates to a diketopyrrolopyrrole derivative of the formula (Ia) ( $B_1$  and  $B_2 = \text{QA}$ )

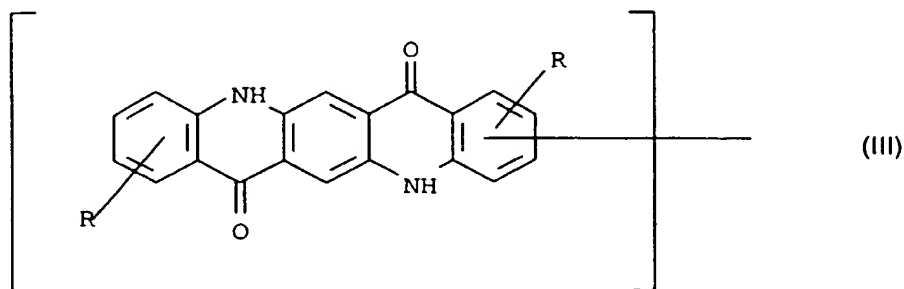


wherein  $A_1$  and  $A_2$  are identical or different aryl radicals, having the meaning given above, and QA is a quinacridone radical; which pyrrolopyrrole derivative is substituted by from 0 to 6 moles of  $-\text{SO}_3\text{M}$  per mole of the pyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation as previously defined.

Preferably, the pyrrolopyrrole derivative is substituted with from 0 to 2 moles of  $-\text{SO}_3\text{M}$  per mole of DPP derivative, most preferably 0 to 0.75 moles of  $-\text{SO}_3\text{M}$  per mole of DPP derivative. Particularly preferred pyrrolopyrrole derivatives contain virtually no  $-\text{SO}_3\text{M}$ .

The preferences described above for  $A_1$  and  $A_2$  apply. In a preferred embodiment of the present invention  $A_1$  and  $A_2$  are phenyl or 4-tertiarybutylphenyl.

QA is preferably a quinacridone radical of the formula (III)



wherein each R is a customary substituent; preferably in the 2 and 9 or 4 and 11 positions.

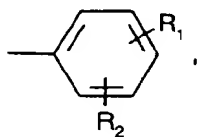
Preferably, each R is independently hydrogen, halogen, carboxyl, unsubstituted C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub> alkyl which is substituted by halogen, unsubstituted C<sub>1</sub>-C<sub>6</sub>alkoxy, or C<sub>1</sub>-C<sub>6</sub>-alkoxy which is substituted by halogen.

Preferably, QA is a quinacridone radical derivable from quinacridone,

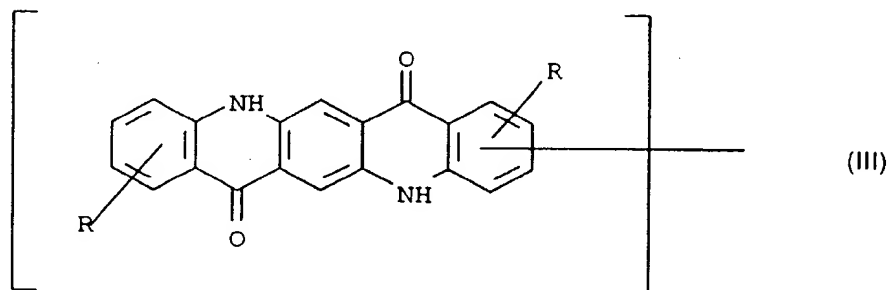
2,9-dichloroquinacridone, 4,11-dichloroquinacridone, 2,9-dimethylquinacridone, 4,11-dimethylquinacridone, 2,9-difluoroquinacridone. Thus, preferred QA substituents are quinacridone radicals of formula (III) wherein each R is hydrogen, Cl, F or -CH<sub>3</sub>. Preferably, if both R substituents are not hydrogen, both R substituents are the same and selected from the group consisting of Cl, F or -CH<sub>3</sub> and most preferably in the 2, 9 or 4, 11 positions. Alternatively, both R substituents are hydrogen.

Especially important compounds are those wherein A<sub>1</sub> and A<sub>2</sub> are identical and are selected from the group consisting of phenyl, 4-methylphenyl, 4-tert-butylphenyl, 4-chlorophenyl, 4-bromophenyl and biphenyl-1-yl (4-phenylphenyl); especially those compounds wherein both R substituents on the QA radical of formula (III) are hydrogen.

In a particularly preferred embodiment of the present invention, the most preferred compounds are those pyrrolopyrrole derivatives of formula (Ia) wherein A<sub>1</sub> and A<sub>2</sub> are each a group of formula

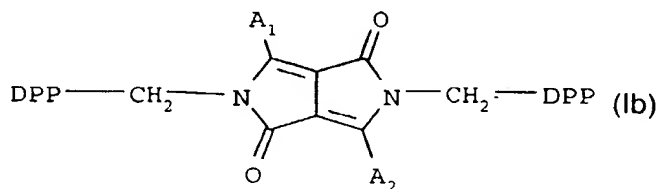


wherein R<sub>1</sub> and R<sub>2</sub> are each independently of the other hydrogen, methyl, tert-butyl, chloro, bromo, phenyl or CN; and QA is a radical of the formula



wherein the R substituents are hydrogen, 2,9- or 4,11-dichloro, 2,9- or 4,11-difluoro or 2,9- or 4,11-dimethyl.

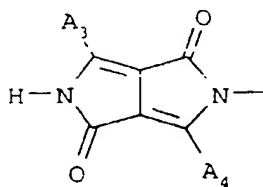
Another preferred aspect of the present invention relates to a pyrrolopyrrole derivative of the formula (Ib) (B<sub>1</sub> and B<sub>2</sub> = DPP)



wherein A<sub>1</sub> and A<sub>2</sub> are identical or different aryl radicals, having the meaning given above, and DPP is a diaryldiketopyrrolopyrrole radical; which diketopyrrolopyrrole derivative is substituted by from 0 to 6 moles of -SO<sub>3</sub>M per mole of the pyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation.

Preferably, the pyrrolopyrrole derivative is substituted with from 0 to 2 moles of -SO<sub>3</sub>M per mole of DPP derivative, most preferably 0 to 0.75 moles of -SO<sub>3</sub>M per mole of DPP derivative. Particularly preferred pyrrolopyrrole derivatives contain virtually no -SO<sub>3</sub>M.

Preferably, DPP is a diaryldiketopyrrolopyrrole radical of the formula



wherein  $A_3$  and  $A_4$  are aryl radicals and have the same meaning as  $A_1$  and  $A_2$  which are defined above.

The preferences described above for  $A_1$  and  $A_2$  apply, too, for  $A_3$  and  $A_4$ .

Preferred compounds are those wherein  $A_1$  and  $A_2$  are identical and are selected from the group consisting of phenyl, 4-methylphenyl, 4-tert-butylphenyl, 4-chlorophenyl, 4-bromophenyl and biphenyl-1-yl (4-phenyl-phenyl), especially those wherein  $A_3$  and  $A_4$  are also identical and selected from the group consisting of phenyl, 4-methylphenyl, 4-tert-butylphenyl, 4-chlorophenyl, 4-bromophenyl and biphenyl-1-yl.

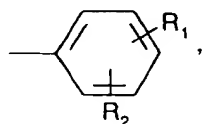
A preferred class of pyrrolopyrrole derivatives are those wherein  $A_3$  and  $A_4$  are each 4-tertbutylphenyl; especially those wherein  $A_1$  and  $A_2$  are identical and selected from phenyl, 4-tertbutylphenyl and 4-methylphenyl; especially 4-tertbutylphenyl. Such pyrrolopyrrole derivatives provide excellent rheology improvement properties when incorporated into a pigment composition, but additionally provide enhancement of desirable pigment properties such as hiding (opacity) and color saturation. Thus, the pyrrolopyrrole derivative wherein  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are each 4-tertbutylphenyl represents an especially preferred compound of the present invention.

Another preferred class of pyrrolopyrrole derivatives are those wherein  $A_3$  and  $A_4$  are each 4-methylphenyl; and  $A_1$  and  $A_2$  are identical and selected from the group consisting of phenyl, 4-tertbutylphenyl and 4-methylphenyl; especially 4-tertbutylphenyl.

The pyrrolopyrrole derivatives of the present invention are especially suitable for use as rheology-improving agents for organic pigments. As rheology-improving agents for organic pigments, the inventive pyrrolopyrrole derivatives function to reduce the viscosity of a dispersion of the pigment composition in a high-molecular-weight organic material, such as a coating composition, for example, a water-borne or solvent-borne automotive paint.

Thus, another aspect of this invention relates to pigment compositions which comprise an organic pigment and a pyrrolopyrrole derivative of formulae (I, Ia and/or Ib). Preferably, the pigment composition contains from 0.1 to 20 percent by weight of the pyrrolopyrrole derivative. Most preferably, the pigment composition contains from 1 to 10 percent by weight of the pyrrolopyrrole derivative.

Preferably, the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) is selected such that  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are each a group of formula



wherein  $R_1$  and  $R_2$  are each independently of the other hydrogen, methyl, tert-butyl, chloro, bromo, phenyl or CN. At least one of  $R_1$  and  $R_2$  is preferably hydrogen. Most preferably, at least one of  $R_1$  and  $R_2$  is hydrogen and the other is in the 3- or 4-position of the phenyl ring.

Important pigment compositions according to the present invention are those which contain a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole pigment or a quinacridone pigment as the organic pigment including their solid solutions and a pyrrolopyrrole derivative of the formulae (I, Ia and/or Ib).

The inventive pigment compositions especially include those containing a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole pigment selected from the group consisting of unsubstituted 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole, 1,4-diketo-3,6-di(3- or 4-chlorophenyl)pyrrolo[3,4-c]pyrrole, 1,4-diketo-3,6-di(3,4-dichlorophenyl)pyrrolo[3,4-c]pyrrole, 1,4-diketo-3,6-di(3-cyanophenyl)pyrrolo[3,4-c]pyrrole, 1,4-diketo-3,6-di(4-tert-butylphenyl)pyrrolo[3,4-c]pyrrole, 1,4-diketo-3,6-di(4-methylphenyl)pyrrolo[3,4-c]pyrrole, and 1,4-diketo-3,6-di(biphenyl-1-yl)pyrrolo[3,4-c]pyrrole, and a pyrrolopyrrole derivative of formulae (I, Ia and/or Ib).

In addition, the inventive pigment compositions especially include those containing a quinacridone pigment selected from the group consisting of unsubstituted quinacridone, 2,9- and 4,11-dimethylquinacridone, 2,9- and 4,11-dichloroquinacridone and 2,9- and 4,11-difluoroquinacridone and a pyrrolopyrrole derivative of formulae (I, Ia and/or Ib).

Especially important pigment compositions are those containing a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole pigment selected from the group consisting of unsubstituted 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole and 1,4-diketo-

3,6-di(4-tert-butylphenyl)pyrrolo-[3,4-c]pyrrole in combination with a pyrrolopyrrole derivative of formulae (I and/or Ia), and/or of formula (Ib) wherein  $A_3$  and  $A_4$  are each 4-tert-butylphenyl, especially those wherein in addition  $A_1$  and  $A_2$  are identical and selected from phenyl, 4-tert-butylphenyl and 4-methylphenyl; especially 4-tert-butylphenyl, most preferred, if the organic pigment is red or orange colored, or wherein  $A_3$  and  $A_4$  are each 4-methylphenyl, especially those wherein in addition  $A_1$  and  $A_2$  are identical and selected from phenyl, 4-tert-butylphenyl and 4-methylphenyl; especially 4-tert-butylphenyl.

Although the pigment compositions of the present invention can consist of only the organic pigment and the pyrrolopyrrole derivative, the pigment compositions generally contain customary additives, such as texture improving agents, light stabilizers and especially a second rheology-improving agent. In this application, the expression "pigment composition" preferably means a formulation which is to be dispersed in a high-molecular-weight organic material that is composed of the pigment, the pyrrolopyrrole derivatives and any optional additives.

Useful light stabilizers are U.V. light absorbers, for example, benzotriazoles or hindered amine light stabilizers (HALS).

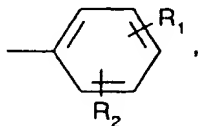
Texture-improving agents are especially useful as an additional component which can improve the properties of the stir-in pigment compositions. Suitable texture-improving agents include fatty acids having at least 12 carbon atoms, and amides, esters or salts of fatty acids. Typical fatty acid derived texture-improving agents include fatty acids such as stearic acid or behenic acid, and fatty amines such as lauryl amine, or stearylamine. In addition, polyols, such as aliphatic 1,2-diols or polyvinyl alcohol, and ethoxylated fatty alcohols, epoxidized soya bean oil, waxes, resin acids and resin acid salts are suitable texture-improving agents. Rosin acids and rosin acid salts are especially suitable texture-improving agents. In general, the inventive pigment compositions contain from 0 to 20 percent by weight of the texture improving agent, preferably 0.5 to 10 percent by weight.

Agents useful as the second rheology-improving agent in the present pigment compositions include quinacridone derivatives, such as, quinacridone sulfonic acid, or a salt thereof, especially the aluminum salt, or pyrazolylmethyl-quinacridone, or other pyrrolopyrrole (DPP) derivatives, such as, a DPP sulfonic acid, or a salt thereof, or a another DPP derivative of the formula I. If the pigment composition includes a second rheology-improving agent, the combined parts by weight of the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) and the second rheology-improving agent are preferably in the range from 0.2 to 20 parts by weight per part of the pigment; most preferably from 2 to 10 parts per part of the pigment.

As discussed above, the presence of an inventive pyrrolopyrrole derivative in a dispersion of an organic pigment in a high-molecular-weight organic material effectively reduces the viscosity of the dispersion. Thus, the present invention further relates to a method of reducing the viscosity of a dispersion of an organic pigment in a high-molecular-weight organic material which comprises incorporating an effective viscosity-reducing amount of a pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) into the dispersion.

The pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) is added to the dispersion on its own, or, preferably, as a component of a pigment composition.

Preferably, the pyrrolopyrrole derivative of formula (Ib) is chosen such that  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are each a group of formula



wherein  $R_1$  and  $R_2$  are each independently of the other hydrogen, methyl, tert-butyl, chloro, bromo, phenyl or CN. At least one of  $R_1$  and  $R_2$  is preferably hydrogen. Most preferably, at least one of  $R_1$  and  $R_2$  is hydrogen and the other is in the 3- or 4-position of the phenyl ring.

Preferably, the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) is present in the dispersion in an amount in the range from 0.1 to 20 parts by weight per part of the pigment dispersion. Preferably, the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) is present in the dispersion in an amount in the range from 0.2 to 10 parts by weight per part of the pigment dispersion. If the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) is combined with a second rheology-improving agent, the combined parts by weight of the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) and the second rheology-improving agent are preferably in the range from 0.1 to 20 parts by weight per part of the pigment dispersion; most preferably from 0.2 to 10 parts per part of the pigment dispersion.

The organic pigment is an azo, azomethine, anthraquinone, phthalocyanine, perinone, perylene, 1,4-diketo-3,6-di-arylpyrrolo[3,4-c]pyrrole, thioindigo, isoindoline, isoindolinone, quinacridone, flavanthrone, indanthrone, anthrapyrimidine and quinophthalone pigments; in particular a 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole or quinacridone pigment, or a mixture thereof.

The high-molecular-weight organic materials are, for example, cellulose ethers, cellulose esters, polyurethanes, polyesters, polycarbonates, polyolefins, polystyrene, polysulfones, polyamides, polycycloamides, polyimides, polyethers, polyether ketones, polyvinyl halides, polytetrafluoroethylene, acrylic and methacrylic polymers, rubber, silicone polymers, phenol/formaldehyde resins, melamine, formaldehyde resins, urea/formaldehyde resins, epoxy resins and diene rubbers or copolymers thereof.

The dispersions especially contain a high-molecular-weight organic material which is useful for heat-curable or cross-linked coatings, for example chemically-reactive coatings, including stoving finishes which contain the customary binders and which are reactive at high temperature. Examples of the high-molecular-weight organic materials which are used in such coatings include acrylic, alkyd, epoxy, phenolic, melamine, urea, polyester, polyurethane, blocked isocyanate, benzoguanamine or cellulose ester resins, or combinations thereof. The pigmented, high-molecular-weight organic materials prepared according to the present process are also useful as air-drying or physically-drying coatings, for example, conventional lacquers such as those used in the cosmetics industry as nail varnishes, for example nitro-cellulose lacquers.

The present process is particularly suitable for reducing the viscosity of dispersions containing high-molecular-weight organic materials conventionally employed as finishes in the automobile industry, especially acrylic/melamine resin, alkyd/melamine resin or thermoplastic acrylic resin systems, as well as in aqueous-based coating systems.

The use of many of the known viscosity-reducing agents for pigment dispersions often results in at least some loss of saturation when the pigment dispersion is applied as the basecoat in a basecoat/clearcoat automotive finish. However, the use of the present pyrrolopyrrole derivatives of formulae (I, Ia and/or Ib) as viscosity-reducing agents surprisingly does not result in loss of saturation when the pigment dispersion is applied as the basecoat in a basecoat/clearcoat automotive finish, indeed in many instances the saturation of the finish is increased by the presence of the pyrrolopyrrole derivative of formulae (I, Ia and/or Ib).

Thus, the present invention further relates to a method of preparing a basecoat/clearcoat finish, which comprises the step of applying a dispersion comprising an effective viscosity-reducing and saturation-enhancing amount of a pyrrolopyrrole derivative of formulae (I, Ia and/or Ib) in a high-molecular-weight organic compound to a substrate; especially wherein in the compound of formula (Ib)  $A_3$  and  $A_4$  are each 4-tert-butylphenyl; and  $A_1$  and  $A_2$  are identical and selected from the group consisting of phenyl, 4-tertbutylphenyl and 4-methylphenyl; especially 4-tert-butylphenyl.

Another preferred embodiment relates to a method of preparing an basecoat/clearcoat finish, which comprises the step of applying a dispersion comprising an organic pigment and an effective viscosity-reducing amount of a pyrrolopyrrole derivative of formulas (I, Ia, Ib) in a high-molecular-weight organic compound to a substrate.

A preferred embodiment of the present invention relates to a coating composition, such as an automotive finish, which comprises a high-molecular-weight organic material, a red- or orange-colored organic pigment and a pyrrolopyrrole derivative of the formula (Ib) wherein  $A_3$  and  $A_4$  are each 4-tertbutylphenyl; especially those wherein  $A_1$  and  $A_2$  are identical and selected from phenyl, 4-tertbutylphenyl and 4-methylphenyl; especially phenyl or 4-tert.-butylphenyl.

In addition, a preferred embodiment of this invention includes a coating composition, which comprises a high-molecular-weight organic material, a red- or orange-colored organic pigment and a pyrrolopyrrole derivative of the formula (Ib) wherein  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are each phenyl, or  $A_1$  and  $A_2$  are phenyl and  $A_3$  and  $A_4$  are each 4-tert.-butylphenyl.

Preferably, the red- or orange-colored organic pigment is selected from the group consisting of unsubstituted 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole and 1,4-diketo-3,6-di(4-tert.-butylphenyl)pyrrolo[3,4-c]pyrrole.

Preferably, the high-molecular-weight organic material is an acrylic/melamine resin, alkyd/melamine resin or thermoplastic acrylic resin.

Preferences discussed above for the pyrrolopyrrole derivatives relate to all other aspects of this invention.

In this application, the expression "automotive finish" is used to describe finishes typically used for automobiles, such as waterborne and solventborne basecoat/clearcoat finishes. Such finishes are used for numerous applications other than for automobiles, such as other motor vehicles, bicycles, and appliances.

In addition to being useful as an intermediate to prepare the diketopyrrolopyrrole derivatives of formulae (I, Ia and/or Ib), the hydroxymethyl pyrrolopyrrole compound of formula (II) is useful as a stabilizer for polymers.

The diketopyrrolopyrrole derivatives of formulae (I, Ia and Ib) are useful as colorants, such as pigments and dyes, for a variety of materials, in particular paints, plastics and inks, and as additives which influence the rheology characteristics of a pigment composition.

In general, diketopyrrolopyrrole derivatives of formulae (I, Ia and Ib) with a lower degree of sulfonation are most suitable as pigments, while those with a higher degree of sulfonation are useful as dyes and additives.

The following examples further illustrate the preferred embodiments of this invention. In these examples, all parts given are by weight unless otherwise noted. All viscosity measurements are taken at room temperature.

**Example 1:** 500 grams of concentrated sulfuric acid (95.28%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 6.2 grams (0.206 moles) of paraformaldehyde are then introduced into the sulfuric acid followed by 28.8 grams (0.1 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]

pyrrole (unsubstituted DPP) in small portions maintaining the pot temperature below 30°C. The reaction mixture is stirred at 25±2°C for 2.5 hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield 2,5-di (hydroxymethyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dione (analysis  $C_{20}H_{16}N_2O_4$ ).

Examples 2-5: The bis(hydroxymethyl) DPP compounds disclosed in Table 1 are prepared by substituting the appropriate substituted DPP for unsubstituted DPP in the process of Example 1:

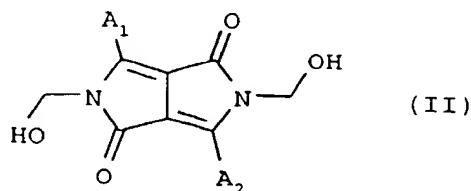


Table-1

Bishydroxymethyl DPP derivatives				
A1	A2	Mol. Form	Mol. Wt	crystallized from
4-Cl-phenyl	4-Cl-phenyl	$C_{20}H_{14}Cl_2N_2O_4$	417	DMF-MeOH
p-tolyl	p-tolyl	$C_{22}H_{20}N_2O_4$	376	DMF-MeOH
4-t-butyl- phenyl	t-butyl-phenyl	$C_{28}H_{32}N_2O_4$	460	DMF-MeOH
biphenyl-1-yl	biphenyl-1-yl	$C_{32}H_{24}N_2O_4$	500	DMF-MeOH

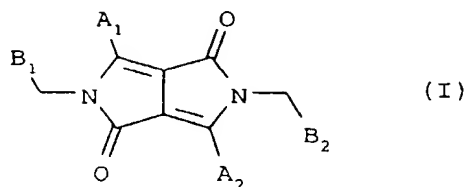
Example 6: 250 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 14.4 grams (0.05 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) are added in small portions maintaining the pot temperature below 25°C. 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture. The reaction mixture is stirred at 25±2°C for four hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield 2,5-di(hydroxymethyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dione (analysis  $C_{20}H_{16}N_2O_4$ ).

Example 7: 401.2 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 17.85 grams (0.05 moles) of 1,4-diketo-3,6-di (4-chlorophenyl)pyrrolo[3,4-c]pyrrole (dichloro DPP) are added in small portions maintaining the pot temperature below 30°C. 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture. The reaction mixture is stirred at 25±2°C for four hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield 2,5-di(hydroxymethyl)-3,6-di(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (analysis  $C_{20}H_{14}Cl_2N_2O_4$ ).

Example 8: 422.9 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 22.0 grams (0.05 moles) of 1,4-diketo-3,6-di (biphenyl-1-yl)pyrrolo[3,4-c]pyrrole (biphenyl DPP) are added in small portions maintaining the pot temperature below 30°C. 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture. The reaction mixture is stirred at 25±2°C for four hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield 2,5-di(hydroxymethyl)-3,6-di(biphenyl-1-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (analysis  $C_{32}H_{24}N_2O_4$ ).

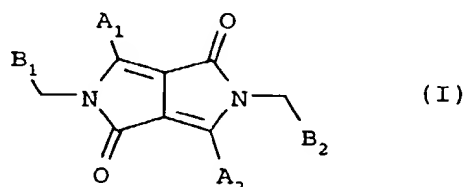
Example 9: 250 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. Quinacridone (31.2 grams, 0.1 moles) is added in small portions followed by 14.4 grams (0.05 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) maintaining the pot temperature between 40-45°C. After stirring for 0.5 hours, 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture and the temperature rises to about 50°C. The reaction is stirred at 45±3°C for 1 hour and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield the compound of the formula





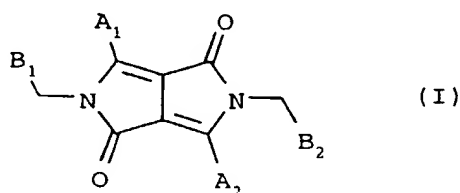
wherein A<sub>1</sub> and A<sub>2</sub> are each phenyl and B<sub>1</sub> and B<sub>2</sub> are quinacridinyl radicals. The product analyzes C<sub>60</sub>H<sub>35.5</sub>N<sub>6</sub>O<sub>6</sub> • (SO<sub>3</sub>H)<sub>0.5</sub>.

**Example 10:** 250 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 14.4 grams (0.05 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) are then added in small portions maintaining the pot temperature below 40°C. After stirring for 0.5 hours, 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture and the temperature rises to about 45°C. The reaction is stirred at 40±2°C for 1 hour. 31.2 grams (0.1 moles) of quinacridone is then added maintaining the temperature below 45°C. The reaction mixture is stirred at 45±2°C for 3 hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield the compound of the formula



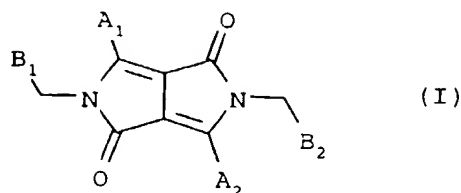
wherein B<sub>1</sub> and B<sub>2</sub> are quinacridinyl radicals. The product analyzes C<sub>60</sub>H<sub>35.5</sub>N<sub>6</sub>O<sub>6</sub> • (SO<sub>3</sub>H)<sub>0.5</sub>.

**Example 11:** 250 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 14.4 grams (0.05 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) are then added in small portions maintaining the pot temperature below 25°C. After stirring for 1 hour, 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture followed by 31.2 grams of quinacridone (0.1 moles) and the maintaining the temperature below 25°C. The reaction mixture is stirred at 25±2°C for 3 hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield the compound of the formula



wherein B<sub>1</sub> and B<sub>2</sub> are quinacridinyl radicals. The product analyzes C<sub>60</sub>H<sub>36</sub>N<sub>6</sub>O<sub>6</sub>.

**Example 12:** 400 grams of concentrated sulfuric acid (96%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 14.4 grams (0.05 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) are then added in small portions maintaining the pot temperature below 25°C. After stirring for 1 hour, 3.1 grams (0.103 moles) of paraformaldehyde are then introduced into the reaction mixture followed by 38.1 grams of 4,11-dichloroquinacridone (0.1 moles) and the maintaining the temperature below 45°C. The reaction mixture is stirred at 45±2°C for 2.5 hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield the compound of the formula

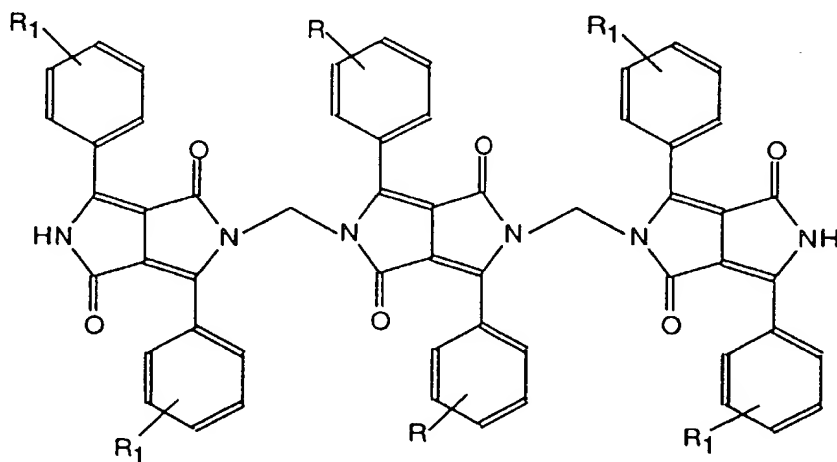


wherein  $B_1$  and  $B_2$  are 4,11-dichloroquinacridinyl radicals. The product analyzes  $C_{60}H_{34}C_{12}N_6O_6$ .

**Example 13:** 500 grams of concentrated sulfuric acid (90%) are added to a one liter fournecked flask equipped with a stirrer, a thermometer and a reflux condenser with a drying tube. 6.2 grams (0.206 moles) of paraformaldehyde are then introduced into the sulfuric acid followed by 28.8 grams (0.1 moles) of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (unsubstituted DPP) in small portions maintaining the pot temperature below  $30^\circ\text{C}$ . The reaction mixture is stirred at  $25 \pm 2^\circ\text{C}$  for 2.5 hours and then poured into ice water, filtered, washed with water until the filtrate is acid free, dried and pulverized to yield a mixture of 2,5-di(hydroxymethyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dione and the starting materials. When 85%  $H_2SO_4$  replaces the 90%  $H_2SO_4$ , a mixture containing a major portion of the starting materials is obtained.

**Example 14:** 250 grams of concentrated sulfuric acid (96%) and paraformaldehyde (3.3g.; 0.11 moles) are added to a one liter four necked flask, equipped with a stirrer, a thermometer, a reflux condenser with a drying tube. Unsubstituted DPP (14.4g.; 0.05 moles) are added to the sulfuric acid/paraformaldehyde mixture in small portions maintaining the pot temperature between  $25-30^\circ\text{C}$ . This mixture is stirred for 1 hour to ensure complete solution. An additional 200g of sulfuric acid is then added to the reaction mixture followed by unsubstituted DPP (28.8g.; 0.1 moles) in small portions, maintaining the pot temperature at  $32-34^\circ\text{C}$ . This reaction mixture is then stirred at  $30 \pm 3^\circ\text{C}$  for 4 hrs and poured into icewater, filtered, washed with water until the filtrate is acid free, dried and pulverized.

The compound isolated analyzed for  $C_{56}H_{36}N_6O_6$  and is believed to have the formula IV



wherein each R and  $R_1$  substituent is hydrogen.

The compounds in Table 2 are made by substituting the appropriate pyrrolopyrrole reactants in the process of Example 14.

TABLE 2

DPP-CH <sub>2</sub> -DPP-CH <sub>2</sub> -DPP derivatives			
R	$R_1$	Mol. Form	crystallized from
H	H	$C_{56}H_{36}N_6O_6$	$H_2SO_4$
H	Cl	$C_{56}H_{32}Cl_4N_6O_6$	$H_2SO_4$
H	CH <sub>3</sub>	$C_{60}H_{44}N_6O_6$	$H_2SO_4$
H	t-Butyl	$C_{72}H_{68}N_6O_6$	$H_2SO_4$
H	4-Phenyl	$C_{80}H_{52}N_6O_6$	$H_2SO_4$

TABLE 2 (continued)

DPP-CH <sub>2</sub> -DPP-CH <sub>2</sub> -DPP derivatives			
R	R <sub>1</sub>	Mol. Form	crystallized from
Cl	H	C <sub>56</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
Cl	Cl	C <sub>56</sub> H <sub>30</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
Cl	CH <sub>3</sub>	C <sub>60</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
Cl	t-Butyl	C <sub>72</sub> H <sub>66</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
Cl	4-Phenyl	C <sub>80</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
CH <sub>3</sub>	H	C <sub>58</sub> H <sub>40</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
CH <sub>3</sub>	Cl	C <sub>58</sub> H <sub>36</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>62</sub> H <sub>48</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
CH <sub>3</sub>	t-Butyl	C <sub>74</sub> H <sub>72</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
CH <sub>3</sub>	4-Phenyl	C <sub>82</sub> H <sub>56</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
t-Butyl	H	C <sub>64</sub> H <sub>52</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
t-Butyl	Cl	C <sub>64</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
t-Butyl	CH <sub>3</sub>	C <sub>68</sub> H <sub>60</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
t-Butyl	t-Butyl	C <sub>80</sub> H <sub>84</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
t-Butyl	4-Phenyl	C <sub>88</sub> H <sub>68</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
4-Phenyl	H	C <sub>68</sub> H <sub>44</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
4-Phenyl	Cl	C <sub>68</sub> H <sub>40</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
4-Phenyl	CH <sub>3</sub>	C <sub>72</sub> H <sub>52</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
4-Phenyl	t-Butyl	C <sub>84</sub> H <sub>76</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>
4-Phenyl	4-Phenyl	C <sub>92</sub> H <sub>60</sub> N <sub>6</sub> O <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>

**Example 15:** 250 grams of concentrated sulfuric acid (96%) and paraformaldehyde (3.3g.; 0.11 moles) are added to a one liter four necked flask, equipped with a stirrer, a thermometer, a reflux condenser with a drying tube. Unsubstituted DPP (14.4g.; 0.05 moles) are added to the sulfuric acid/paraformaldehyde mixture in small portions maintaining the pot temperature between 30-35 °C. This mixture is stirred for 1 hour to ensure complete solution. An additional 200g of sulfuric acid is then added to the reaction mixture followed by unsubstituted DPP (28.8g.; 0.1 moles) in small portions, maintaining the pot temperature at 38-42 °C. This reaction mixture is then stirred at 40±3°C for 4 hrs and poured into icewater, filtered, washed with water until the filtrate is acid free, dried and pulverized. The compound isolated analyzed for C<sub>56</sub>H<sub>36</sub>N<sub>6</sub>O<sub>6</sub>·(SO<sub>3</sub>H)<sub>0.5</sub>

The sulfonated derivatives of the compounds of Table 2 are prepared by substituting the appropriate pyrrolopyrrole reactants in the process of Example 15.

**Example 16:** Bishydroxymethyl DPP (17.4g, 0.05 moles), aniline (9.3g, 0.1 moles) and DMF (100ml) are added to a one liter four necked flask, equipped with a stirrer, a thermometer, and a reflux condenser with a drying tube. The mixture is stirred at 100°C for 4 hrs, then diluted with water, filtered, washed with water, dried and pulverized to give 2,5-di(anilinomethyl)-3,6-diphenyl pyrrolo[3,4-c]pyrrole-1,4-dione (bis(anilinomethyl) DPP).

**Example 17:** Bishydroxymethyl DPP (17.4g, 0.05 moles), a catalytic amount of paratoluene sulfonic acid and methanol (100ml) are added to a one liter four necked flask, equipped with a stirrer, a thermometer, and a reflux condenser with a drying tube. The mixture is stirred at reflux for 4 hrs., diluted with water, filtered, washed with water, dried and pulverized to give 2,5-di(methoxymethyl)-3,6-diphenyl pyrrolo[3,4-c]pyrrole-1,4-dione (bismethoxymethyl DPP).

**Example 18:** Bishydroxymethyl-di-t-butyl DPP (23.0g, 0.05 moles), a catalytic amount of paratoluene sulfonic acid and methanol (100ml) are added to a one liter four necked flask, equipped with a stirrer, a thermometer, and a reflux condenser with a drying tube. The mixture is stirred at reflux for 4 hrs, diluted with water, filtered, washed with water, dried and pulverized to give 2,5-di(methoxymethyl)-3,6-di-t-butylphenyl pyrrolo[3,4-c]pyrrole-1,4-dione (bismethoxymethyl di-t-butyl DPP).

**Examples 19-26:** The following compounds, wherein A<sub>1</sub>, A<sub>2</sub> and R are defined according to formulae (Ia) and (III), are prepared according to the procedures of Examples 9-12 by substituting the appropriate DPP and quinacridone compounds:

Ex	A <sub>1</sub>	A <sub>2</sub>	R
19	phenyl	phenyl	2,9-diCl

(continued)

Ex	A <sub>1</sub>	A <sub>2</sub>	R
20	phenyl	phenyl	2,9-diMe
21	phenyl	phenyl	4,11-diMe
22	4-tbu-phenyl	4-tbu-phenyl	2,9-diCl
23	4-Cl-phenyl	4-Cl-phenyl	H
24	4-Me-phenyl	4-Me-phenyl	H
25	4-tbu-phenyl	4-tbu-phenyl	H
26	4-Me-phenyl	4-Me-phenyl	2,9-diCl

**Example 27:** A pigment composition is prepared by adding a surface treating agent which consists of the pyrrolopyrrole derivative of formula (Ia), alone, or combined with a second rheology-improving agent, to an aqueous suspension of the pigment, filtering and washing to yield the pigment composition. The viscosity of a dispersion of the pigment composition in a commercial high solids solvent-borne paint formulation is measured at 50 rpm.

Pyrrolopyrrole Derivative	Second Rheology Improving Agent	Pigment	% by Weight Pigment in Dispersion	P/B	Millbase Viscosity (Brookfield)
none	none	1	10	0.5	1610
8% Example 11	none	1	10	0.5	63
4% Example 11	4% QMA	1	10	0.5	62
4% Example 24	4% PMQA	2	10	0.5	600
4% Example 19	4% PMQA	2	10	0.5	708
4% Example 22	4% PMQA	2	10	0.5	648
4% Example 25	4% PMQA	2	10	0.5	474
4% Example 10	4% QMA	2	10	0.5	736
none	none	3	10	0.5	1910
4% Example 10	4% QMA	3	10	0.5	1210
QMA=quinacridone sulfonic acid, aluminum salt PMQA=pyrrazolylmethylquinacridone 1 =a ternary solid solution of dichloro DPP/DPP/2,9-dichloroQA (48/32/20) 2= binary solid solution of dichloro DPP/2,9-dichloroQA(60/40) 3=1,4-diketo-3,6-di(biphenyl-1-yl)pyrrolopyrrole					

**Example 28:** A solid solution of dichloro DPP/dichloroquinacridone (40/60) is prepared by milling a mixture of the two individual components on a roller for 24 hours and stirring the mill powder with 2% sulfuric acid for 2 hours at 90°C, and then filtering and washing the resulting pigment slurry. The resulting presscake is reslurried in water and combined with the rheology-improving agent(s) specified in the table below, filtered, washed, dried and pulverized to yield a treated pigment. A pigment dispersion containing 10% pigment and 30% solids at a pigment/binder ratio of 0.5 is prepared by combining the treated pigment with acrylourethane resin, dispersant resin and solvent and milling with grinding media for 64 hours. The Brookfield viscosity of the resulting pigment dispersion is reported in the following table.

Pyrrolopyrrole Derivative	Second Rheology Improving Agent	Millbase Viscosity (Brookfield)
4% Example 10	4% PQMA	566
4% Example 24	4% PQMA	600

(continued)

Pyrrolopyrrole Derivative	Second Rheology Improving Agent	Millbase Viscosity (Brookfield)
4% Example 25	4% PQMA	474
4% Example 26	4% PQMA	708
4% Example 22	4% PQMA	648

**Example 29:** Automotive finishes are obtained by spray painting aluminum panels with a metallic or mica paint formulation prepared by conventional methods and pigmented with the above described pigment compositions. The coatings exhibit attractive, intense colors with excellent two-tone, high gloss and distinctness of image.

**Example 30:** An organic ternary solid solution pigment which is composed of dichloro DPP/-unsubstituted DPP / 2,9-dichloroquinacridone (48% / 32% / 20%), is combined with a rheology-improving agent composed of 4% quinacridone monosulfonic acid, aluminum salt (QMA) and 4% of the pyrrolopyrrole derivative of Example 14 by adding the rheology-improving agent to an aqueous suspension of the pigment, filtering and washing to yield the pigment composition. Rheology profiles of pigment dispersions in a commercial high solids solvent-borne paint formulation containing about 12% by weight of the pigment at a pigment to binder ratio of 0.5% are depicted in the Table 3.

Table 3

MILLBASE VISCOSITY (BROOKFIELD)		
Paint System: BC / CC;	% Pigment: 12.0 %;	P / B = 0.5
Sample ID	Rheology-improving Agent	50 RPM
30a	Untreated	3660
30b	4%QMA+4% Example 14 R=R <sub>1</sub> =H	828

**Example 31:** An orange-colored di(t-butylphenyl)-DPP pigment is combined with a rheology-improving agent described according to formula (IV) given in ex. 14. Rheology profiles of pigment dispersions in a commercial high solids solventborne paint formulation containing about 16% by weight of the pigment at a pigment to binder ratio of 0.5% measured after 4 hours of attritor milling are depicted in the Table 4.

Table 4

Millbase Viscosity (Brookfield)		
sample	Rheology-improving Agent	50 rpm
31a	4% R=H; R <sub>1</sub> =CH <sub>3</sub>	868
31b	8% R=H; R <sub>1</sub> =CH <sub>3</sub>	546
31c	4% R=t-Bu, R <sub>1</sub> =t-Bu	670
31d	8% R=t-Bu, R <sub>1</sub> =t-Bu	528

The rheology-improving of examples 31c and 31d, in addition to the rheology improvements, improves the color saturation of the pigment when sprayed on a panel as part of a conventional basecoat/clearcoat automotive finish. Similarly improved color saturation is observed when a different red or orange pigment, for example quinacridone, is used in place of di(t-butylphenyl)-DPP.

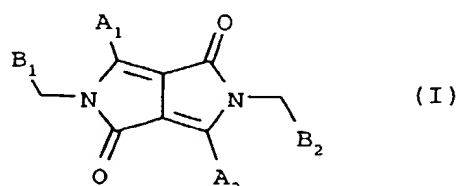
**Example 32:** An orange-colored di(t-butylphenyl)-DPP pigment is combined with the mixture of rheology-improving agents described in the Table 5 with R and R<sub>1</sub> being described according to formula (IV) given in ex. 14 and PYMQ being pyrrazolylmethylquinacridone. Rheology profiles of pigment dispersions in a commercial high solids solventborne paint formulation containing about 16% by weight of the pigment at a pigment to binder ratio of 0.5% measured after 4 hours of attritor milling are depicted in the Table 5.

Table 5

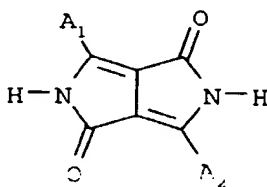
Millbase Viscosity (Brookfield)		
Sample	Rheology-improving Agent	50rpm
32	no treatment	>2000
32a	4% PYMQ + 4% R=H; R <sub>1</sub> =CH <sub>3</sub>	954
32b	4% R=H; R <sub>1</sub> =tBu + 4% R=H; R <sub>1</sub> =CH <sub>3</sub>	1080
32c	2% R=H; R <sub>1</sub> =tBu + 2% R=H; R <sub>1</sub> =CH <sub>3</sub>	1320

# Claims

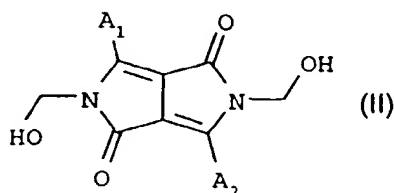
1. A process for the preparation of a diketopyrrolopyrrole derivative of the formula (I)



wherein A<sub>1</sub> and A<sub>2</sub> are identical or different aryl radicals and B<sub>1</sub> and B<sub>2</sub> are identical or different organic radicals; which diketopyrrolopyrrole derivative contains from 0 to 6 moles of -SO<sub>3</sub>M per mole of diketopyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation, which process comprises a reaction wherein a 1,4-diketo-3,6-diarylprrrolopyrrole of the formula

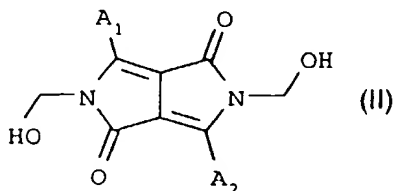


is reacted in a first step with formaldehyde or paraformaldehyde to yield a sulfonated or non-sulfonated intermediate of the formula



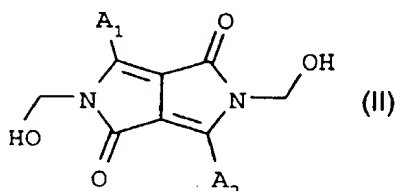
which reacts in a second step with a precursor of the organic radicals, B<sub>1</sub> and B<sub>2</sub>, to yield the diketopyrrolopyrrole derivative of formula (I).

2. A process for the preparation of a diketopyrrolopyrrole derivative of the formula (I) wherein a 1,4-diketo-3,6-diarylpyrrolopyrrole of the formula (II) is reacted with a precursor of the organic radicals,  $B_1$  and  $B_2$ .
3. A process of claim 1 or 2 wherein the precursor of the organic radicals,  $B_1$  and  $B_2$ , is a 1,4-diketo-3,6-diarylpyrrolo [3,4-c]pyrrole or a quinacridone.
4. A compound of the formula

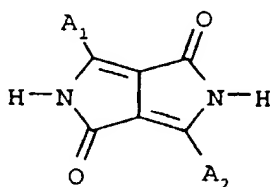


which contains from 0 to 6 moles of  $-SO_3M$  per mole of the compound, wherein  $A_1$  and  $A_2$  are identical or different aryl radicals and M is hydrogen or a metal or ammonium cation.

5. A process for preparing a compound of the formula

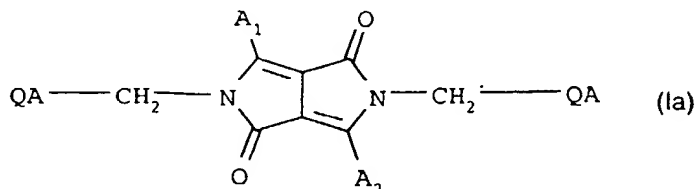


which contains from 0 to 6 moles of  $-SO_3M$  per mole of the compound, wherein  $A_1$  and  $A_2$  are identical or different aryl radicals and M is hydrogen or a metal or ammonium cation, which process comprises reacting a 1,4-diketo-3,6-diarylpyrrolopyrrole of the formula



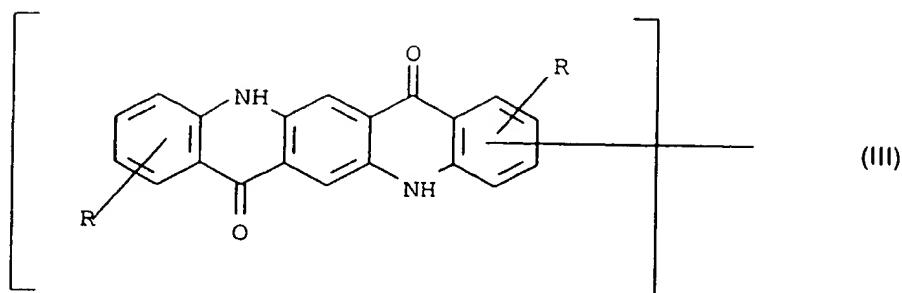
with formaldehyde or paraformaldehyde.

6. A diketopyrrolopyrrole derivative of the formula (Ia)



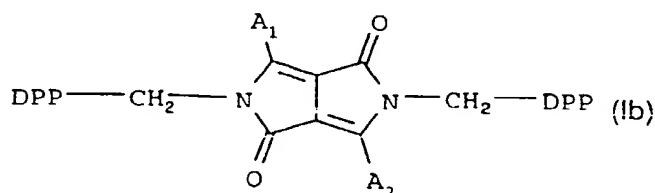
wherein  $A_1$  and  $A_2$  are identical or different aryl radicals, and each QA is a quinacridone radical; which pyrrolopyrrole derivative is substituted by from 0 to 6 moles of  $-SO_3M$  per mole of the pyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation.

7. A pyrrolopyrrole derivative of claim 6 wherein each QA is a quinacridone radical of the formula (III)



wherein each R is independently hydrogen, halogen, carboxyl, unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> alkyl which is substituted by halogen, unsubstituted C<sub>1</sub>-C<sub>6</sub> alkoxy, or C<sub>1</sub>-C<sub>6</sub> alkoxy which is substituted by halogen.

8. A pyrrolopyrrole derivative of the formula (Ib)



wherein A<sub>1</sub> and A<sub>2</sub> are identical or different aryl radicals, and each DPP is a diaryldiketopyrrolopyrrole radical; which diketopyrrolopyrrole derivative is substituted by from 0 to 6 moles of -SO<sub>3</sub>M per mole of the pyrrolopyrrole derivative; wherein M is hydrogen or a metal or ammonium cation.

9. A pigment composition which comprises an organic pigment and a pyrrolopyrrole derivative of formulas (I, Ia, Ib) according to claims 1, 6, 7 or 8.
10. A method of reducing the viscosity of a dispersion of an organic pigment in a high-molecular-weight organic compound, which comprises incorporating an effective viscosity-reducing amount of a pyrrolopyrrole derivative of formulas (I, Ia, Ib) according to claims 1, 6, 7, or 8 into the dispersion.
11. A method of preparing an basecoat/clearcoat finish, which comprises the step of applying a dispersion comprising an organic pigment and an effective viscosity-reducing amount of a pyrrolopyrrole derivative of formulas (I, Ia, Ib) according to claims 1, 6, 7, or 8 in a high-molecular-weight organic compound to a substrate.
12. A method of preparing an basecoat/clearcoat finish, which comprises the step of applying a dispersion comprising an effective viscosity-reducing and saturation-enhancing amount of a pyrrolopyrrole derivative of formulas Ib according to claims 8 in a high-molecular-weight organic compound to a substrate.



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 811 625 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
08.04.1998 Bulletin 1998/15

(51) Int Cl.<sup>6</sup>: C07D 487/04, C07D 519/00,  
C09B.57/00  
// (C07D487/04, 209:00, 209:00)

(43) Date of publication A2:  
10.12.1997 Bulletin 1997/50

(21) Application number: 97810324.0

(22) Date of filing: 27.05.1997

(84) Designated Contracting States:  
CH DE ES FR GB IT LI NL

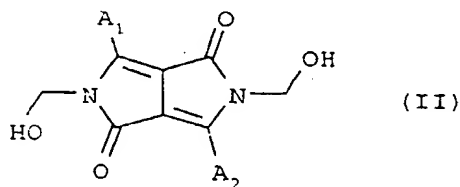
(71) Applicant: Ciba Specialty Chemicals Holding Inc.  
4057 Basel (CH)

(30) Priority: 05.06.1996 US 19138 P  
26.09.1996 US 27469 P  
26.09.1996 US 27470 P

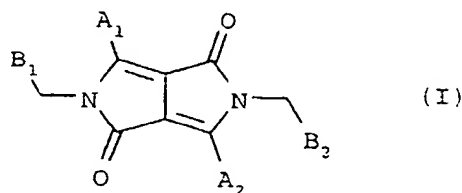
(72) Inventor: Hendi, Shivakumar Basalingappa  
Newark, DE 19702 (US)

(54) Process for preparing diketopyrrolopyrrole derivatives

(57) This disclosure relates to a process for preparing bis(hydroxymethyl)pyrrolopyrrole compounds of the formula



wherein A<sub>1</sub> and A<sub>2</sub> are aryl radicals, by reacting a 1,4-diketopyrrolopyrrole with formaldehyde or paraformaldehyde. The compound of formula (II) can be isolated or further reacted in a one pot synthesis to yield a compound of the formula



wherein B<sub>1</sub> and B<sub>2</sub> are organic radicals.

EP 0 811 625 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 97 81 0324

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 224 445 A (CIBA GEIGY AG) * the whole document *	1-12	C07D487/04 C07D519/00 C09B57/00 /(C07D487/04, 209:00,209:00)
A	EP 0 648 770 A (CIBA GEIGY AG) * claims *	1-12	
D.A	EP 0 133 156 A (CIBA GEIGY AG) * claims *	1-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07D C09B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 February 1998	Examiner Henry, J
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention F: earlier patent document, but published on or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background U: non-written disclosure I: intermediate document			

EPO FORM 1503 (3/82) (P.O.C.H.)